

erally employed in the form of a contiguous bed wherein the particles are in contact with surrounding particles.

In a preferred mode of carrying out the process of this invention, an aqueous solution to be treated is passed through a column containing a fluid-permeable granular aggregate of the cross-linked gel polymer. The flow of the solution may be upward or downward. The flow may be actuated by gravity, pumps or application of vacuum. Aggregates of fine-dimensioned polymer granules will generally afford greater absorption efficiency but impose greater resistance to fluid passage than coarse particle aggregates. This is particularly true in the case of polymer having high water absorption. It has been found that, in general, the preferred range of the ratio average granule size/water absorption value is between .002 and .5 wherein average granule size is expressed in inches as determined from a sieving operation using the U.S. Bureau of Standards Screen Series, and the water absorption value is the ratio of wet polymer weight to dry polymer weight. For example, a bed of 270 mesh polymer granules, namely particles which pass through a 270 mesh screen but are retained by the next finer screen, having an average granule size of .0021 inch, provides practical linear flow rate of solution passing therethrough when the water absorption value is below 1. In a bed of granules of 0.1 inch size, the polymer may have a water absorption of 20 with securement of practical fluid permeability and efficient absorption.

Column beds are preferably prepared in such manner as to avoid entrapment of air within the column and to prevent channeling. The polymer granules may be mixed with similarly dimensioned particles of other materials to enhance flow or absorption, or to secure other special effects. In one embodiment of the present invention, the polymer granules are mixed with granules of activated carbon. The advantage of such combination is that, in a solution treating operation wherein both the polymer and carbon have similar absorptive affinities for a chromophoric substance, the polymer gel serves as a visual indicator of the progress of absorption. This permits replacement or regeneration of the absorbent before it saturates with the absorbed solute.

The polymer gel absorbs from aqueous solution many large-molecule organic compounds, especially those containing chromophoric groups or active hydrogen atoms, and also absorbs polyvalent heavy metal cations such as copper, iron, nickel and cobalt, and certain anions. The strength or retentiveness of absorption varies with the specific polymer and specific solute. Many substances, once absorbed, can be removed or eluted from the polymer by treatment of the polymer with large amounts of the pure solvent from which the solute was originally absorbed, or by treatment of the polymer with a different solution. Certain absorbed organic materials may be removed by treatment with permanganate or other oxidant. In this manner, the polymer can in many cases be re-used and the absorbed solute can be recovered free of the polymer gel. In the case of treatments of solutions containing a number of solutes, more than one of which absorbs on the gel, the absorbed solutes can generally be preferentially desorbed via appropriate elution treatment and thereby separated from each other. For example, if both nickel and cobalt are absorbed onto a gel made from nitrilotriacetic acid and ethylene diamine, the cobalt can be separately eluted by flowing a large volume of pure water through the gel. Similarly, if copper and iron are absorbed on the same gel, iron can be eluted with dilute HCl. In multicomponent absorption and elution in a column, the several components may form distinct zones or bands on the column, thus facilitating visual observation and controlled separation.

In other modes of carrying out the process of this invention, the polymer gel in granular form may be slurried with the aqueous solution to be treated, and the

mixture separated by filtration, sedimentation, or flotation. In another mode, the gel granules may be enclosed within a porous screen envelope which may then be immersed in a flowing stream of solution to be treated or dragged through a relatively stationary solution. In still another mode, the gel granules may be sintered together to form a self supporting, fluid permeable structure, or the granules may in some other manner be converted into a rigid structure, for example by incorporation within a fluid permeable matrix such as an open sponge or fibrous structure or by co-sintering with another material.

The weight of solute absorbable by the gel is dependent upon the solute, the specific gel, and the conditions of absorption. Some polymer gels can absorb a weight of solute equal to their own weight. Granular polymer aggregates of this invention, containing an absorbed substance can be employed in applications where the polymer serves as a slow release substrate for the absorbate. Thus, the polymer may serve as a carrier for odorants, insecticides, herbicides, bactericides, desiccants, catalysts, oxidant and the like and as a general carrier for liquid compounds which must be utilized in non-liquid form. Metal ions absorbed by the polymer may be reduced to lower valence states by treatment of the granules with reducing agents such as sodium borohydride, sodium hypophosphite and sodium hydrosulfite.

Although not wishing to be bound by theoretical interpretations, it is felt that the unique absorbency characteristics of the cross-linked gel polymer are due to critical effects of hydrogen bonding, dipole interactions, and spatial configuration within the molecular geometry. These factors presumably cause the polymer to exhibit unusual chelation affinities. It is noteworthy that all the polymers contain recurring tertiary amino nitrogen atoms and recurring amide groups. It has also been found that, all other factors being equal, polymers containing alkylene radicals of more than 2 carbons, as may be obtained via use of propylene diamine monomer, lack the necessary gel properties. It is felt that the affinity of the polymer for certain organic compounds is attributable in part to the gel structure which functions to some extent in the manner of a molecular sieve to entrap molecules of certain dimensions.

A further understanding of my invention will be had from a consideration of the following examples which illustrate certain preferred embodiments. All parts and percentages are by weight unless otherwise indicated. Examples A, B and C exemplify methods for the preparation of various polymers which may be employed in the practice of the present invention.

#### EXAMPLE A

A mixture of 180 parts ethylene diamine and 100 parts distilled water containing 4.5 parts sodium sulfite are slowly added by a dropping funnel to a refluxing solution of 250 parts nitrilotriacetoneitrile dissolved in 650 parts of distilled water. The rate of addition is adjusted so as to maintain controlled rapid evolution of ammonia. The system is sealed except for a valve which permits egress of ammonia. Following complete addition of the ethylene diamine solution, the mixture is refluxed for 4½ hours. Water is then removed from the mixture over a 6 hour period by azeotropic distillation with toluene. The temperature rises to about 120° C. and the mixture becomes highly viscous. The flask is cooled slightly and the reaction product, a light yellow rubbery substance, is removed. Upon cooling, it solidifies to a non-brittle yellow glass. The product is purified by leaching in water, whereupon the polymer becomes soft and swollen. Upon drying, the polymer is obtained in brittle form having a pale amber color.

The washed and dried polymer is found to absorb 1.7 times its weight of water when immersed in water at 25° C. The polymer is insoluble in the usual solvents for polymers and does not melt prior to decomposition,